Enhanced thermoelectric performance of SnSe based composites with carbon black nanoinclusions

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Abstract

Recently, single crystalline SnSe and its sodium doped compound were reported to have an ultralow thermal conductivity and high thermoelectric figure of merit. However, the highest high thermoelectric figure of merit for polycrystalline SnSe-based materials is not larger than unity. In this study, we report a high thermoelectric figure of merit 1.21 at 903K along the hot pressing direction for polycrystalline SnSe, realized by incorporating a proper proportion of carbon black as nano-inclusions. The exceptional performance arises from the ultra-high power factor, which comes from a high electrical conductivity and an enhanced Seebeck coefficient through energy-dependent scattering.

1. **Introduction**

Thermoelectric effects enable direct coversion between thermal and electrical energy, which can be used for recycling of waste energy. Devices using thermoelectric materials are being used in power generation and refrigeration[1]. Because of energy efficiency, management and conservation, the search for high-performance thermoelectric materials with low cost and earth abundant elements is attracting significant attention. The performance of thermoelectric materials can be evaluated with the dimensionless figure of merit, $ZT=S^2\sigma T/(\kappa_C+\kappa_L)$,

where Z is figure of merit and T is absolute temperature, S, σ, κ_C and κ_L are Seebeck coefficient, electrical conductivity, carrier thermal conductivity and lattice thermal conductivity[2,3]. The good thermoelectric materials should have high Seebeck coefficient, high electrical conductivity by electrionic structure modification[4-7] or low thermal conductivity by phonon scattering at grain boundaries [8-11].

Very recently, the surprising high record ZT≈2.6 and 2.3 at 923K along the *b* and *c*-axis were reported by Zhao et al in p-type SnSe single crystal[12], which was arised from the intrinsically ultralow thermal conductivity due to strong anharmonicity of the chemical bonds. A record high ZT_{dev} of 1.34, with ZT ranging from 0.7 to 2.0 at 300-773K, was realized in sodium doped SnSe single crystals[13]. However, due to the long duration of synthesis and the poor mechanical properties for layered single-crystalline SnSe, TE properties of polycrystalline SnSe materials were studied. As one of IV-VI compounds, SnSe with narrow band-gap has a layered structure with orthorhombic pnma space at room temperature. Around 773K, it undergoes a phase transition from pnma space to cmcm space group. Sassi et al[14] reported the thermoelectric properties of polycrystalline SnSe and obtained the maximum ZT of 0.5 at 820 K. The value was significantly lower than those measured in single crystal SnSe due to higher κ and lower σ. However, for polycrystalline SnSe-based material, ZT was not over unity. ZT of 0.6 was reported for polycrystalline SnSe doped with Ag at 750K by Cheng-Lung Chen et al[15], and a *n*-type polycrystalline $SnS_{0.1}Se_{0.8}I_{0.03}$ was obtained with maximum ZT of 1.0 at about 773 K[16].

Nanoscale inclusions in bulk materials can dramatically suppress the lattice thermal conductivity[17]. Theoretical and experimental results also indicate that interface potentials in the nanocomposites with

semiconducting or metallic nanoinclusions can cause enhanced S through energy filtering effect (EFE) [18]. Here we report that by embedding carbon black nanocrystals in bulk SnSe matrix, proper heterojunction potentials bring about strong energy filtering effect giving rise to increased S at elevated temperatures, which results in the improvement of PF. The highest PF value reaches 9.58 $\mu Wcm^{-1}K^{-2}$, 9.63$\mu Wcm^{-1}K^{-2}$ and 8.8 $\mu Wcm^{-1}K^{-2}$ for f=1.5 vol.%, 2.5 vol.% and 3.5 vol.% , respectively, which is 68%, 69% and 54% larger than that of SnSe. The highest ZT value achieved is 1.21 for f=2.5 vol% at 903 K, which outperforms any reported polycrystalline SnSe-based materials. The present study demonstrates CB/SnSe is a promising candidate as a thermoelectric material in the middle temperature range.

2. Experimental

Polycrystalline SnSe alloys were synthesized by direct reaction of stoichiometric amount of Tin shot and Se powders (99.999%, Alfa Aesar) in evacuated and sealed quartz tubes. The tube then was heated up to 1223K over 10 h, and kept for 24 hours, followed by furnace-cooling to room temperature. Then the obtained ingots were ground into powder with an agate mortar.

High quality nano-carbon black powders were obtained by the incomplete combustion or thermal decomposition of natural gas or petroleum oil. Polycrystalline SnSe and carbon black were ground with an agate mortar, and then hot-pressed at 673K under the pressure of 600Mpa in a diameter of 15 mm tungsten carbide die in vacuum for 1 h. The heating rate was 7 K/min. The concentration of carbon black was varied from 1.5 % to 3.5% volume fraction in polycrystalline SnSe, with the theoretical density 6.18g cm^{-3} of SnSe and 1.70g cm^{-3} of carbon black. The relative densities of specimens were between 94-98%. The thermoelectric data has

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obtained from measured three samples: two of the same batch and two of the different batches of samples. The variation in thermoelectric properties for different batches and the same batch of samples is within experimental error.

The samples were characterized by X-ray diffraction (XRD) using Philips X'Pert PRO X-ray diffractometer equipped with graphite monochromatic Cu K_α radiation (λ=1.54056 Å). The operation voltage and current were kept at 40 kV and 40 mA, respectively. The microstructure was characterized by field emission scanning electron microscopy (FESEM; SU8020) with secondary electrons selected to produce the SEM images.

The Seebeck coefficient and electrical resistivity were measured by commericial equipmemnt (ZEM-3(M10), Ulvac Riko, Inc.) in a low-pressure helium environment with samples of about 2 mm×3 mm×10 mm. The thermal conductivity was calculated from $\kappa=dC_pD$. The density d is measured by Archimedes' method. The specific heat C_p is determined by using differential scanning calorimetry (Netzsch DSC 404F3). The thermal diffusivity D is measured by the laser flash method (Netzsch, LFA-457). The Hall coefficient (R_H) was measured using Van Der Pauw method under a reversible magnetic field of 1.5T. The hall carrier concentration (p) and hall mobility (μ) of the charge carriers were calculated from the relations $p=1/(R_He)$ and $\mu=R_H/p$, where e is the electric charge. The uncertainty for the electrical conductivity is 3%, the Seebeck coefficient 5%, the thermal conductivity 7%, so the combined uncertainty for the power factor is 10% and that for ZT value is 12%. Error bars are not shown in the figures to increase the readability of the curves.

3. Results and Discussion

The bulk XRD patterns for fCB/SnSe composite samples (f =0, 1.5, 2.5

and 3.5 *vol*.%) are shown in Fig. 1. The main diffraction peaks correspond to the standard SnSe phase (JCPDS No.89-0233), indicating that the specimens have the same crystallographic structure as the SnSe phase. Weak extra line can be seen in the XRD pattern (inset of Fig. 1) for *f*CB/SnSe composite samples (*f* =0, 1.5, 2.5 and 3.5 *vol*.%) around 2theta = 28 degree, which corresponds to a secondary phase of SnO with JCPDS No.13-0111.

The morphology of carbon black (Fig. 2(a)&(b)) is poly-integrated botryoidal structure with sizes of 40-80nm. Fractographs of the 2.5*vol*.%CB/SnSe composite bulk samples are shown in Fig. 2(c)&(d), from which one can see that there are many black spots with sizes of approximately 40–80 nm distributed among the big gray grains. By further careful inspection with energy dispersive X-ray spectroscopy (EDX), one finds that these areas contain the elements C, Sn and Se (Fig 2(e)). All these indicate that carbon black is incorporated into the SnSe matrix, forming SnSe-CB bulk nanocomposites.

Fig. 3 show the electrical properties of carbon black composite SnSe measured along the hot pressing direction.The temperature dependence of the electrical conductivity of composite samples *f*CB/SnSe (*f* =0, 1.5, 2.5 and 3.5 *vol*.%) is plotted in Fig 3(a). The electrical conductivity of SnSe is much lower than those of the traditional state-of-the-art thermoelectric materials such as PbTe, PbSe, and Cu_2Se[19-22]from 300K to 700K. Over the entire temperature range, the electrical conductivity of pure SnSe monotously increases, showing typical semiconductor transport behavior. In the case of the composite samples the electrical conductivity first increases with temperature, and then decreases quickly with further increasing temperature. In addition, the electrical conductivity of the composite samples is significantly influenced by the

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addition of carbon black. For instance, σ for the composite samples f CB/SnSe (f=1.5, 2.5 and 3.5vol.%) is larger than that of pure SnSe in the whole temperature range investigated.

The S values for the composite samples fCB/SnSe (f=1.5, 2.5 and 3.5vol. %) as shown in Fig. 3(b) are positive, indicating that they are p-type semiconductors and/or the majority of the carriers are holes. The temperature behaviors of S for the composite samples fCB/SnSe (f=0,1.5, 2.5 and 3.5 vol.%) are similar: with increasing temperature S increases in the temperature range of 300-400K and 500-600K; it decreases in the temperature range of 400-500K and 600-800K, leaving a pit in the temperature range of 400-600K, then from 800K to 880K, S is kept unchanged and above 880K S increases with further increasing temperature. The Seebeck coefficient decreases in the temperature range of 600-800K originating from the thermal excitation of the carrier. The pit is observed in the temperature range from 400 to 600K for the pure SnSe and its carbon black composites, however, this phenomenon is not found for single crystal sample, which may be due to the contribution of defect levels, lying close to the edge of valence band, while there are no defect levels in a perfectly crystalized single crystal.

In order to discuss the effect of carbon black on the transport properties of SnSe, carrier concentration p and carrier mobility μ as a function of temperature are given in Fig. 3(c)&(d). Seen from Fig. 3(c), p for pure SnSe increases from 5.78×10^{16}cm^{-3} at 296K to 1.43×10^{19}cm^{-3} at 824K; however, p decreases to 1.25×10^{19}cm^{-3} as the temperature is further increased to 852K. In the case of the composite samples f CB/SnSe (f=1.5, 2.5 and 3.5vol.%), p increases over the measured temperature range. The increase in carrier concentration with temperature is caused by the thermal excitation of majority carriers; while the decrease in p may be

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attributed to the annihilation of majority carriers by the excitation of minority carriers. The carrier mobility μ for all samples as shown in Fig. 3(e) decreases proportionally to $T^{-1.5}$ in the temperature range from 300 to 650K, most likely because the dominant mechanism of carrier scattering is mere acoustic phonon scattering with simple single parabolic band model.

Seen from Fig. 3(d), carrier mobility in the temperature range of 300-600K is nearly unchanged with addition of carbon black, hence, the increase in electrical conductivity with addition of carbon black as compared with that of pure SnSe in 300-600K results largely from the increased carrier concentration as seen in Fig, 3(c). The measurements of carrier concentration and the derived mobility indicate that the great increases in σ for the composite samples fCB/SnSe (f=1.5, 2.5 and 3.5$vol.$%) as compared to pure SnSe in the temperature ranging from 600 to 900K is not only due to the increase of carrier concentration, but also attributed to the enhanced carrier mobility.

Mott formula tells us that S decreases with increasing p. So it's easy to understand that the decrease in Seebeck coefficient with increasing carbon black content in temperature range of 300-600K is originated from the increased carrier concentration. An interesting phenomenon at T>800K is observed in Fig. 3(b) that no reduction or even the larger S for the composite samples than pure SnSe. This phenomenon could be related to the energy filtering effect (EFE) caused by the incorporation of carbon black nanoparticles. When carbon black nanoparticles are dispersed in SnSe matrix, a heterojunction potential (barrier) will be formed at the interfaces due to the different chemical potentials of the two semiconductors. This could cause energy-dependent scattering (EFE) [18], as manifested by the increase of the scattering parameter λ that is usually

related to relaxation time τ by the relation: $\tau = \tau_0 E^{\lambda-1/2}$ (here E is the energy of carriers and τ_0 is energy-independent constant). By using a parabolic band model with acoustic phonon scattering approximation to understand the change of transport properties, the density of state effective mass m_d^* and S can be expressed as:[23]

$$(1)$$

$$(2)$$

with Fermi integral of order i

$$(3)$$

where h and ξ_F are the Planck constant and the reduced Fermi level $F_f/(k_BT)$, respectively. Due to the acoustic scattering is dominant in SnSe (i.e. $\lambda=0$ for $f=0$), we obtain $m_d^*=0.6347m_e$ (T=850 K) (where m_e is the free electron mass) for SnSe. Assuming m_d^* does not change in different samples, the estimated λ is 2.54, 1.90 to 4.0 with increasing f from 1.5, 2.5 to 3.5 *vol.%*. This increase in λ results in 60, 19 and 57 μV/K increase above an expected value in S at 850 K for the samples with f =1.5, 2.5, and 3.5 *vol.%*, respectively, as shown in Fig. 3(f) the dependence of S with p calculated by using Eqs. (1)–(3), where the solid line is Pisarenko relation[24].

The calculated power factor as a function of temperature is shown in Fig. 4(a). One can see that PF of the composite samples increases with increasing temperature from 300 to 800K. About 800K, the composite samples preserve a high power factor, which is attributed to the increase of both electrical conductivity and S at elevated temperatures. The maximum power factor for polycrystalline SnSe is 5.7 μWcm^{-1}K^{-2} at 915K. The power factor for the composite samples is significantly

improved. The highest value reaches 9.58 μWcm^{-1}K^{-2}, 9.63μWcm^{-1}K^{-2} and 8.8 μWcm^{-1}K^{-2} for f=1.5 *vol*.%, 2.5 *vol*.% and 3.5 *vol*.% , respectively, which is 68%, 69% and 54% larger than that of SnSe.

The total thermal conductivity κ_{tot} along the hot pressing direction as a function of temperature for fCB/SnSe (f =0, 1.5, 2.5 and 3.5 *vol*.%) is shown in Fig. 4(b). For all the samples, one can see that κ_{tot} decreases, then increases and further decreases with increasing temperature.When the temperature is blew 773K,the total thermal conductivity of samples decrease with temperature due to the increased phonon–phonon Umklapp scattering (U-scattering). When the temperature is over 773 K, the thermal conductivity quickly startes to increase, which is related to the phase transition from Pnma space group to Cmcm space[25-27].A minimun thermal conductivity of 0.66 Wm^{-1}K^{-1} was obtained for undoped SnSe perpendicular to the hot pressing direction. It is worthwhile to note that the κ_{tot} fureture decrease after 823K,which may due to the existence of an interfacial potential that scatters more electrons than holes. Moreover, it can be seen from Fig. 4(b) that κ_{tot} increases monotonically with the increasing carbon black content due to the inherent large lattice thermal conductivity k_L (>2WK^{-1}m^{-1}) of carbon black[28-29].The lattice thermal conductivity k_L can be obtained by removing the carrier component κ_C from k_{tot} using Wiedemann–Franz relation $k_C = L_0 T \sigma$, where L_0 is the Lorenz number (1.5×10^{-8} V^2 K^{-2}). The calculated ($\kappa_{tot} - L_0 T \sigma$) for fCB/SnSe (f =0, 1.5, 2.5 and 3.5 *vol*.%) are plotted in Fig. 4(c).

The figure of merit ZT of all the samples is shown in Fig. 4(d). Peak ZT for the pure SnSe reaches the maximum of 0.78 at 910K, which is significant higher than that (ZT$_{max}$=0.5) of polycrystalline SnSe reported by S. Sassi[14]. The larger ZT in this work can be attributed to optimizing the carrier concentration by appropriate control of stoichiometric

composition. One can see that ZT for f=1.5 *vol.*%, 2.5 *vol.*% and 3.5 *vol.*% are larger than that of pure SnSe above 800K, reaching 1.20, 1.21 and 1.0 at 903K, respectively, which are 52%, 55% and 28% higher than that of pure SnSe sample.

4. Conclusions

In summary, the thermoelectric properties of composite samples f CB/SnSe (f=0, 1.5, 2.5 and 3.5*vol.*%) have been studied in the temperature range from 300K to 910K. The results show that the incorporation of carbon black nanoparticles into the SnSe matrix can result in an increase in the PF. The increase in the PF is a result of enhanced carrier concentration and enhanced high-temperature S by energy filtering effect. As a result, maximum ZT of 1.21 is achieved in the composite system with f=2.5*vol.*% alone the pressing direction. This study has demonstrated that the thermoelectric performance of SnSe can be effectively improved by incorporating an appropriate quantity of carbon black and CB/SnSe is a promising candidate as a thermoelectric material in the middle temperature range.

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Figure Caption

Fig. 1 XRD patterns for composite samples f CB/SnSe (f=0, 1.5, 2.5 and 3.5 vol.%)

Fig. 2 SEM images of carbon black particles (a)&(b) and the fractured surface of the bulk sample for 2.5vol.%CB/SnSe(c)&(d), EDS spectrum of 2.5vol.%CB/SnSe(e)

 Fig. 3 Temperature dependence for composite samples f CB/SnSe (f =0, 1.5, 2.5 and 3.5 vol.%) (a) electrical conductivity σ; (b) Seebeck coefficient S; (c) carrier concentration p; (d) carrier mobility μ;(e) logμ– logT plots for composite samples; (f) Variation of the Seebeck coefficient with carrier concentration for f CB/SnSe (f =0, 1.5, 2.5 and 3.5 vol.%) at 850 K (The solid line is Pisarenko relation for SnSe at 850 K.)

Fig. 4 Temperature dependent (a) power factor PF; (b) thermal conductivity κ_{tot}; (c) lattice thermal conductivity (κ_{tot}-LTσ) (d) figure of merit ZT for f CB/SnSe (f =0, 1.5, 2.5 and 3.5 vol.%) .

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